



# Vanadium-lithium alumina a potential additive for coke oxidation by CO<sub>2</sub> in the presence of O<sub>2</sub> during FCC catalyst regeneration



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## ABSTRACT

The possibility of performing the regeneration of spent fluid catalytic cracking catalysts in rich CO<sub>2</sub> atmosphere can simultaneously reduce greenhouse gas emissions and produce CO for sequential uses. Herein alumina modified by vanadium and lithium was revealed a remarkable catalyst (or additive) for this goal. High CO<sub>2</sub> conversion was observed in the presence of helium (for instance at 720 and 800 °C, 39 and 76% of CO<sub>2</sub> was converted during the first 5 min of reaction respectively) and it was reduced by less than 5% in the presence of oxygen. Moreover the catalyst works effectively regardless the coke type on spent catalyst, i.e. produced by means of hydrocarbon or bio feed cracking. This catalyst was tested as an additive and works properly up to one part to ten of spent USY. By means of either labeled CO<sub>2</sub> or coke (both with carbon 13) it was shown that primary <sup>13</sup>CO<sub>2</sub> forms <sup>13</sup>CO followed by oxygen mobility between alumina and USY promoting coke oxidation. <sup>12</sup>CO<sub>2</sub> formed in-situ similarly to <sup>13</sup>CO<sub>2</sub> readily reacts with coke producing CO. These effects improve the coke burning by CO<sub>2</sub> and remarkably increase the CO/CO<sub>2</sub> ratio even in the presence of O<sub>2</sub>. Finally these results strongly support that the FCC regeneration step can be kept under auto-thermal condition in CO<sub>2</sub> rich atmosphere.

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## 1. Introduction

Most modern societies are based on capital goods (most of them with scheduled obsolescence) and on energy demands. These features are directly related to greenhouse gas emissions due to the large amount of energy required, mainly provided by burning fossil fuels. Therefore Global warming is a timely topic and the reason of it being anthropogenic (or not) is not a relevant question, as the energy demand has increased continually to supply the energy required for all Human being activities. Therefore our worst choice would be “to wait and see”.

A powerful strategy that can largely contribute to sustainability is to improve the amount of bio-resources coupling with CO<sub>2</sub> uses for fuel production in the standard refinery structure. This strategy comprises a renewable source; CO<sub>2</sub> capture (to CO production) and yet high investment in new processes is not required. Besides it

potentially mitigates greenhouse gas emissions [1,2] this strategy mimics nature in its several cyclic processes.

The possibility of performing spent catalysts regeneration in rich CO<sub>2</sub> atmosphere under Fluid Catalytic Cracking (FCC) process conditions [3,4], simultaneously combines CO<sub>2</sub> capture with CO production for sequential uses, i.e. hydrogen [5,6], methanol [7,8], dimethylether [9,10] or hydrocarbons [11,12] production. Coke formation is a consequence of hydrocarbon cracking reactions on FCC catalyst [13]; the coke amount in the spent catalyst is related to the processed feed, i.e. lower quality feeds or bio-feed that result in greater coke formation in the spent catalyst [4,14,15]. CO<sub>2</sub> and coke reaction (Reverse-Boudouard reaction—RB) are currently present in gasification processes where, for example, alkaline metals are added to coke in order to promote this reaction [16,17]. In dry catalytic reforming hydrogen is supplied by hydrocarbons (formed on metal particles) while simultaneously CO<sub>2</sub> reacts with coke (resulting from hydrogen production) improving the catalyst regeneration [18]. In a previous work we have demonstrated that spent catalysts can be regenerated in CO<sub>2</sub>/O<sub>2</sub> atmosphere in the presence of spent alumina modified by both group I, II elements and vanadium under realistic FCC conditions [19,20]. As CO<sub>2</sub> and coke reaction (Reverse-Boudouard reaction, RB) changes from slightly to largely

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endothermic, depending on the extent of the reaction, auto-thermic conditions for RB reaction can only be achieved in the presence of  $O_2$ . Therefore the goal to use  $CO_2$  as oxidant is to overcome  $O_2$  reactivity that is at least two orders of magnitude higher [17,21]. Thus the coke burnt by oxygen can supply the energy required for  $CO_2$  and coke reaction (in the regeneration step of the FCC); simultaneously providing energy to the overall process thus maintaining the heat balance. Simultaneously, the formation of oxygenated species on the coke surface (Coke-O) can provide the energy required for the partial reduction of  $CO_2$  with coke producing  $CO$ , as supported on the bases of the enthalpy of formation for several oxygenated compounds [22].

The fluid catalytic cracking process (FCC) converts high weight molecular hydrocarbon fractions to gasoline, olefin gases and other products [23]. This process has been adapted to process a broad range of bottom feeds [24–26]. There is a large amount of data in the literature devoted to convert biomass-derivate compounds in FCC.

In terms of lignocellulosic biomass conversion into fuels thermo-conversion of biomass into bio-oil, i.e. pyrolysis [26–28] shows simple hardware and flexibility in terms of feed pyrolysis process. The resulting bio-oil is highly acidic, composed of poly-aromatic and unstable compounds; therefore the resulting bio-oil requires sequential hydrogen treatment (HDO process) to improve its properties [29–31]. Alternatively to that biomass thermo-conversion performed in the presence of a catalyst (CPO process) also improves the bio-oil quality [32,33]. Several approaches to produce green fuel have been attempted, including the use of pure pyrolysis bio-oil [29,34], its mixture with hydrocarbons [32,35,36] and previously hydrogenated pyrolysis bio-oil [15]. For all cases the amount of coke formed in the catalyst increased compared with a feed free from biomass derivate compounds.

Recently an alternative to the aforementioned fuel production based on second-generation biomass was proposed [37]. Bio-crude was obtained by a combination of acid catalyzed hydrolysis of biomass with organic reactions, such as ketalization [37] and acetylation reactions [38]. The catalytic cracking conversion of bio-crude resulted in the production of aromatic compounds capable of being introduced in the gasoline pool [37]. However this strategy resulted in a slight increase of the coke amount [37]. Therefore, it is important to verify the impact of the coke nature on the RB reaction.

The addition of group I and II elements and vanadium to the typical FCC catalyst is out of question, as they act as poisons [39]. For that reason this catalyst has to be tested as an additive to proper application in standard FCC process.

Herein, we explore the RB reaction over alumina modified by lithium and vanadium as catalyst and additive mixed up with spent USY in wt% proportions from 1:1 to 1:0.05, respectively. Yet, this reaction was explored in the presence of  $O_2$  and using different coke types, i.e. coke obtained from vacuum gasoil or oxygenated compounds. Finally,  $^{13}CO_2$  as well as coke (labeled in all carbon 13) were used in order to provide insights into the reaction pathway.

## 2. Experimental

### 2.1. Catalyst preparation and spent catalysts

#### 2.1.1. Reverse-Boudouard catalysts/additives

The alumina ( $Al_2O_3$ ) used as support for all catalysts used in this work was obtained by calcination of bohemite (diffraction pattern JCPDS 74-1985) for 20 h at  $800^\circ C$  under air atmosphere. Lithium was impregnated on the alumina support through the incipient wetness technique using LiCl (99%, VETEC) as precursor. The amount of LiCl used in the impregnation was determined to obtain 5 wt.% Li. After impregnation the sample was dried over

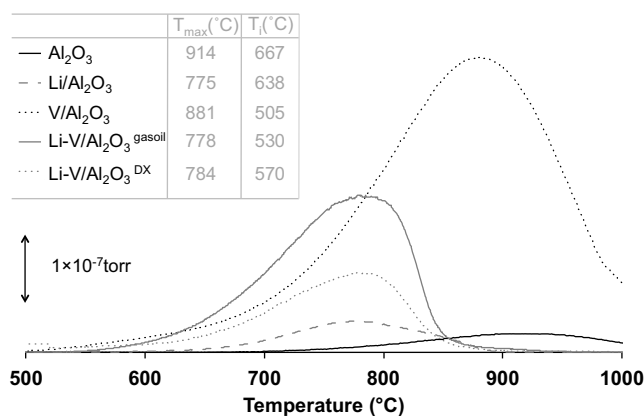


Fig. 1. CO formation profile under increasing temperature ( $10^\circ C \text{ min}^{-1}$ ) and 10%  $CO_2/He$  atmosphere.  $T_{max}$  and  $T_i$  represent temperature for maximum CO formation and temperature at which CO begins to be formed.

night at  $120^\circ C$ . The  $Li/Al_2O_3$  catalyst was obtained by calcination of the dried impregnated alumina at  $800^\circ C$  for 20 h under air atmosphere.

Vanadium was added to  $Li/Al_2O_3$  and  $Al_2O_3$  in order to obtain the  $V-Li/Al_2O_3$  and  $V/Al_2O_3$  catalysts respectively. Vanadium was impregnated on the referred supports by using an aqueous solution of vanadyl acetylacetonate (Vanadium(IV)-oxyacetylacetonate, VAA, Aldrich, 95 wt.%). 25 mL of solution per gram of catalyst. The samples were placed in contact with the VAA solution and heated at boiling temperature until all water had dried. The remaining solids were dried at  $120^\circ C$  overnight and thermal treated at  $600^\circ C$  for 3 h under air atmosphere. The catalyst preparation was performed to obtain a loading of 1% of vanadium.

#### 2.1.2. Acid catalyst (USY)—catalytic cracking active phase

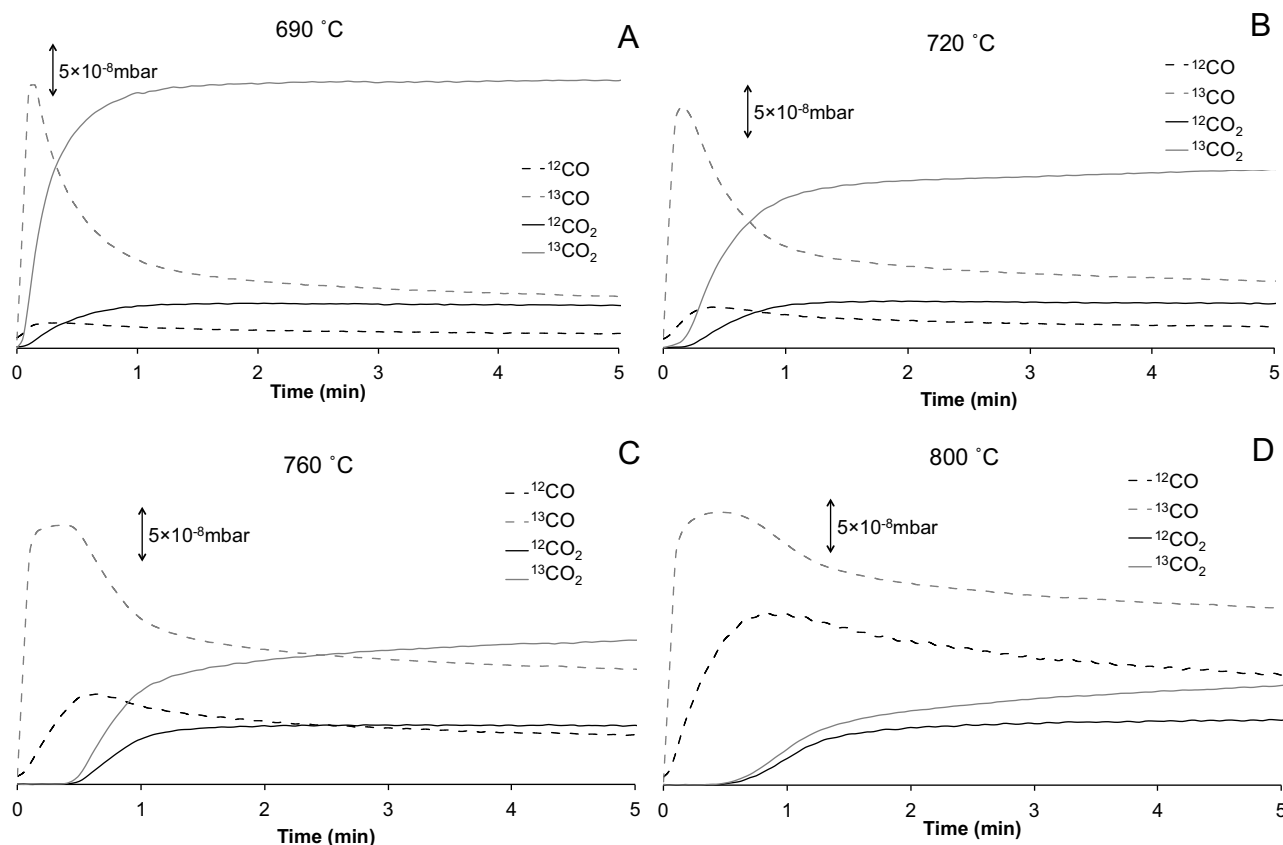
Na-USY ( $SAR = 13$ ,  $S_{BET} = 605 \text{ m}^2 \text{ g}^{-1}$ ,  $V_{micropore} = 0.24 \text{ cm}^3 \text{ g}^{-1}$ ) zeolite was gently supplied by PETROBRAS. The acid form of the zeolite was obtained by performing ion exchange using a  $(NH_4)_2SO_4$  1 M solution (20 mL per gram of zeolite) at  $70^\circ C$  for 1 h. The ion exchange procedure was performed 4 times to completely eliminate any trace of sodium. Afterwards, the sample was dried overnight at  $120^\circ C$  and thermal treatment at  $500^\circ C$  for 4 h under air.

### 2.2. Samples coking

Two different types of coke in spent catalyst were used in this study. The first resulted from the catalytic cracking of vacuum gasoil and the second from the catalytic cracking of 1,2:3,5-di-O-isopropylidene- $\beta$ -D-xylofuranose (10 wt.%) in *n*-hexane (99%, VETEC). In order to differentiate the samples, gasoil and DX indexes were added to the catalysts name respectively for coking with vacuum gasoil and 1,2:3,5-di-O-isopropylidene- $\beta$ -D-xylofuranose (10 wt.%) in *n*-hexane.

#### 2.2.1. Vacuum gasoil coke

Prior to coking the samples were impregnated with a vacuum gasoil/*n*-hexane mixture with a weight proportion of 1 gasoil for 2 of catalyst. The *n*-hexane amount was the minimum required to dissolve all vacuum gasoil. The samples were added to the gasoil/*n*-hexane mixture and stirred at room temperature until complete *n*-hexane evaporation, after which the sample was heated at  $120^\circ C$  overnight. The sample was then heated at  $530^\circ C$  for 15 min under nitrogen flow ( $60 \text{ mL min}^{-1}$ ).



**Fig. 2.**  $^{12}\text{CO}$ ,  $^{13}\text{CO}$ ,  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  profiles for the Reverse-Boudouard reaction of gasoil coke deposited on the Li-V/ $\text{Al}_2\text{O}_3$  surface with  $^{13}\text{CO}_2$  (1.9%)/He at 690 °C (A), 720 °C (B), 760 °C (C) or 800 °C (D).

### 2.2.2. 1,2:3,5-di-O-Isopropylidene- $\beta$ -D-xylofuranose (DX) coke

Previous to coking the samples were heated at 500 °C ( $10^\circ\text{C min}^{-1}$ ) under nitrogen flow ( $100\text{ mL min}^{-1}$ ). Once 500 °C attained,  $0.2\text{ mL min}^{-1}$  of a mixture of 10% DX in *n*-hexane was fed at the entrance of the reactor during 15 min, in addition to the  $100\text{ mL min}^{-1}$  nitrogen flow. 500 mg of catalyst was used each time. The coked sample was then cooled until room temperature under nitrogen flow ( $100\text{ mL min}^{-1}$ ).

### 2.2.3. Spent USY using regular carbon isotopic distribution and labeled coke in all carbon 13

The first spent USY resulted from the catalytic cracking of 1,2:3,5-di-O-isopropylidene- $\beta$ -D-xylofuranose (10 wt.%) in *n*-hexane (previously described procedure) and the second from the fructose labeled in all carbons ( $^{13}\text{C}_6$ -fructose, 99%, Omicron Biochemicals Inc.). The second type of spent USY as prepared using  $^{13}\text{C}_6$ -Fructose (Fructose labeled in all carbons) that resulted in a spent USY with coke labeled in all carbon. The USY zeolite and the labeled fructose were mixed together in a weight proportion of 2:1. Afterwards the mixture was heated at 500 °C for 15 min under a nitrogen flow of  $100\text{ mL min}^{-1}$ .

### 2.3. Catalyst characterization

Textural characterization was carried out in a Micromeritics ASAP 2010. Initially, the catalysts were pretreated at 200 °C under vacuum during 2 h, then the isotherms of adsorption of nitrogen at 77 K were performed and specific surface area was determined through the BET method. X-ray powder diffraction (XRD) patterns were obtained using a Rigaku X-ray diffractometer with nickel-filtered  $\text{CuK}\alpha 1$  radiation source ( $\lambda = 0.15406\text{ nm}$ ) and

graphite monochromator. The XRD profiles were collected in the  $2\theta$  angle region between  $5^\circ$  and  $80^\circ$ , at a step width of  $0.05^\circ$ , counting 1 s between each step. The patterns of all catalysts, i.e.  $\text{Al}_2\text{O}_3$ , Li/ $\text{Al}_2\text{O}_3$ , V/ $\text{Al}_2\text{O}_3$  and V-Li/ $\text{Al}_2\text{O}_3$ , are presented in Supplementary information Fig. S1. The samples loading in Lithium and Vanadium were obtained using a Philips PU 7000 ICP-AAS. XPS analyses were performed to obtain the surface composition of the catalysts. The XPS analyses were performed on an Escalab 250 XI Thermo Scientific equipment, with an AlK $\alpha$  monochromatic radiation of 1486.6 eV and at pressure of  $1 \times 10^{-9}$  mbar. The spent catalysts coke loading was determined through thermogravimetric analysis in a Netzsch TG-IRIS equipment. The samples were dried under a  $\text{N}_2$  flow at 250 °C for 30 min (heating rate of  $10^\circ\text{C min}^{-1}$ ). Afterwards, the sample was heated to 700 °C under airflow at heating rate of  $10^\circ\text{C min}^{-1}$ . The coke loading corresponded to the samples weight loss under airflow.

### 2.4. Reverse-Boudouard reaction

The spent catalysts were submitted to two experimental procedures as described below. In all cases the formed gases were monitored by on-line Mass Spectrometer MKS (model PPT430). In the first experimental procedure the mass spectra were collected continuously during the sample (100 mg) heating from 25 °C to 1000 °C at a heating rate of  $10^\circ\text{C min}^{-1}$  under a 10%  $\text{CO}_2$  in Helium flow of  $60\text{ mL min}^{-1}$ . In the second experimental procedure the spent catalysts (100 mg) were heated from 25 °C to the reaction temperatures (690, 720, 760, 800 °C) at a heating rate of  $10^\circ\text{C min}^{-1}$  under a He flow of  $60\text{ mL min}^{-1}$  and kept under these conditions until the mass spectra profiles stabilized. Once stabilized the He

flow was switched to a  $30 \text{ mL min}^{-1}$  flow of one of the following atmospheres:  $^{13}\text{CO}_2$  (1.9%) in He and  $^{13}\text{CO}_2$  (1.9%)/ $\text{O}_2$  (0.8%) in He.

Independently of the reaction atmosphere the amounts of  $^{12}\text{CO}$  and  $^{13}\text{CO}$  on the present profiles were corrected in consideration of the fragmentation of  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$ , respectively, into CO. This fragmentation is typical of the Mass Spectrometer and it was empirically estimated that CO formed through fragmentation corresponds to 8% of the  $\text{CO}_2$  signal.

### 3. Results and discussion

#### 3.1. Catalyst characterization

The properties of the catalysts are described in Table 1. Total vanadium and lithium loading were similar in both  $\text{V}/\text{Al}_2\text{O}_3$  and  $\text{Li-V}/\text{Al}_2\text{O}_3$ . In contrast metal loadings based on XPS results largely differ from that of bulk composition. Lithium is largely distributed on surface and yet when both lithium and vanadium were present ( $\text{Li-V}/\text{Al}_2\text{O}_3$  catalyst) lithium amount increased 23% compared to that of  $\text{Li}/\text{Al}_2\text{O}_3$  (from 5.6 to 6.8 respectively) while vanadium decreased 50% (from 0.4 wt.% to 0.2 wt.%).  $\text{Li}/\text{Al}_2\text{O}_3$  catalyst showed a large decrease of surface area and pore volume compared to pristine alumina. On the other hand, vanadium caused no modification on the textural properties. The surface area reduction observed after Lithium impregnation was most likely due to the formation of the spinel phase  $\text{LiAl}_5\text{O}_8$  (XRD pattern is presented in Supplementary information Fig. S1), which correlated well with the higher superficial lithium amount. Vanadium is probably located in bulk lithium chemical environment thus resulting it being less detectable by XPS. Yet, it is important to notice that the vanadium coverage of the surface in  $\text{Li-V}/\text{Al}_2\text{O}_3$  catalyst is 35 times smaller than that of Lithium.

The coke amount formed by regular vacuum gasoil feed was different among spent catalysts and was affected both by textural properties (larger surface areas enable higher coke loadings) and by the type of alumina modification (by adding lithium, vanadium or both). This can be clearly observed when comparing  $\text{Al}_2\text{O}_3$  and  $\text{V}/\text{Al}_2\text{O}_3$ , where the amount of coke increased two-fold despite both catalysts showing similar surface area. Vanadium seemed to have a higher impact on coke production than lithium as, according to XPS results, it only covered a very small portion of the samples surface. Indeed, vanadium has been proven to increase coke formation during catalytic cracking reaction [40]. In order to minimize the impact of textural properties coke amount is also presented as its percentage per catalyst area (determined by BET), Table 1. The presence of lithium and vanadium individually increased coke produced by vacuum gasoil by 140% and 70% respectively compared to pristine alumina and when combined ( $\text{Li-V}/\text{Al}_2\text{O}_3$  catalyst) coke amount remarkably increased 250%.

In addition to the vacuum gasoil feed, coke was also produced on spent  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  by using a mixture of 1,2:3,5-di-*O*-isopropylidene- $\beta$ -D-xylofuranose 10 wt.% in *n*-hexane (gasoil a DX indexes were used for differentiation when necessary). As expected the different feeds led to different coke amounts being deposited on the catalyst surface, respectively 3.9% and 6.4% for the coke resulting for vacuum gasoil and 1,2:3,5-di-*O*-isopropylidene- $\beta$ -D-xylofuranose.

The type of oxygenated functional groups present in the coke was analyzed qualitatively through comparison the CO and  $\text{CO}_2$  profiles observed under helium flow with literature [41] and are presented in Fig. S2 and Table S1 and by  $^{13}\text{C}$  NMR Figs. S5 and S6. It could be possible to infer the presence of lactone, carboxylic acid, quinone, carbonyl and phenol functional groups in the coke produced by DX or gasoil cracking in the former technic.  $^{13}\text{C}$  NMR showed similar results for  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{Gasoil}}$  and  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  cat-

alysts, and the latter showed less intensity signal in the carbonyl region compared to the former. Both technics suggest that coke is similar in terms of composition in both spent  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{Gasoil}}$  and  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$ . Another important feature is that the type of catalyst did not significantly affect both the coke functionality and the intensity of CO and  $\text{CO}_2$  profiles, since the presence of oxygenated species on the coke surface affects RB reaction. Kelemen and Freund demonstrated that on glassy carbon surfaces  $\text{CO}_2$  activation was more difficult to occur when oxygenated species are present on the surface [17].

#### 3.2. Temperature programmed of oxidation in $\text{CO}_2$ (TPO- $\text{CO}_2$ )

A preliminary study aiming to determine the temperature range of the Reverse-Boudouard (RB) reaction was carried out on spent catalysts by studying the CO formation profile under increasing temperature (Fig. 1). Firstly the CO intensity was quite different between samples; this was most likely due to the different amounts of coke deposited on the samples surface. The temperature of maximum CO formation ( $T_{\text{max}}$ ) ranged from  $775^\circ\text{C}$  to  $914^\circ\text{C}$  according to the following order:  $\text{Li}/\text{Al}_2\text{O}_3^{\text{Gasoil}} \approx \text{Li-V}/\text{Al}_2\text{O}_3^{\text{Gasoil}} \approx \text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}} \ll \text{V}/\text{Al}_2\text{O}_3^{\text{Gasoil}} < \text{Al}_2\text{O}_3^{\text{Gasoil}}$ . Therefore, the results in Fig. 1 show that lithium, either in the presence of vanadium or by itself, had a much higher influence on decreasing the maximum CO formation temperature ( $T_{\text{max}}$ ) than vanadium.

The temperatures at which CO started to be formed ( $T_i$ ) are presented in Fig. 1.  $\text{V}/\text{Al}_2\text{O}_3^{\text{Gasoil}}$  and  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{Gasoil}}$  presented a similar performance with  $T_i$  differing only 5%. The initial CO formation temperature ( $T_i$ ) followed the order  $\text{V}/\text{Al}_2\text{O}_3^{\text{Gasoil}} \approx \text{Li-V}/\text{Al}_2\text{O}_3^{\text{Gasoil}} < \text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}} < \text{Li}/\text{Al}_2\text{O}_3^{\text{Gasoil}} \approx \text{Al}_2\text{O}_3^{\text{Gasoil}}$ . The results observed for  $T_i$  and  $T_{\text{max}}$  suggest that  $\text{Li-V}/\text{Al}_2\text{O}_3$  is the most promising catalyst to perform the Reverse-Boudouard reaction under FCC regenerator conditions, i.e. lower  $T_{\text{max}}$  or  $T_i$  when compared to the catalysts modified by either lithium or vanadium. Indeed previous studies have shown that when alkaline metals supported on alumina were doped with vanadium their performance for promoting the Reverse-Boudouard reaction is significantly enhanced [19,20]. The effect of coke loading cannot be ruled-out, as it is 50% superior in  $\text{V}/\text{Al}_2\text{O}_3^{\text{Gasoil}}$ . However, on the bases of the remarkable effect on  $T_i$  and  $T_{\text{max}}$  caused by the type of catalyst, it is expected for RB reaction to be more affected by the catalyst rather than the coke amount and/or nature. As prove of conception for this statement Reverse-Boudouard was carried out (and compared) in both spent  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  and spent  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{Gasoil}}$ . RB reaction in spent  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  resulted in a slight increase on  $T_i$  compared to  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{Gasoil}}$ , however both catalysts showed similar  $T_{\text{max}}$ , i.e. respectively  $784^\circ\text{C}$  and  $778^\circ\text{C}$ . Despite moderate differences in coke amount in both catalysts the results clearly demonstrate minor effect in CO profiles and it should be proposed that  $\text{Li-V}/\text{Al}_2\text{O}_3$  catalyst is effective in promoting the Reverse-Boudouard reaction regardless the coke nature and amount. For example hydrogen from coke is mostly released as  $\text{H}_2$  during heating from room temperature to the reaction temperature resulting in  $\text{H}_2/\text{CO}$  ratio (MS spectrometer signal) around  $10^{-4}$  (Table S3). Similarly water is barely observed simultaneously to CO, as presented in Fig. S4, resulting in low  $\text{H}_2\text{O}/\text{CO}$  ratios (around  $10^{-2}$ ). This is related to the decomposition of hydrogen in the coke previously or simultaneously to Reverse-Boudouard reaction, a condition imposed by experimental set-up. Under realistic FCC unit the catalyst is directly transferred from the riser to the regenerator resulting in high amount of hydrogen in the coke of the spent catalyst. It was previously demonstrated that aliphatic carbons easily reacts with oxygen compared to more condensed carbons [42] one could expect the same behavior when oxygen is provided by  $\text{CO}_2$  in partial RB reaction. As a consequence the results presented in this manuscript are conservative as fast

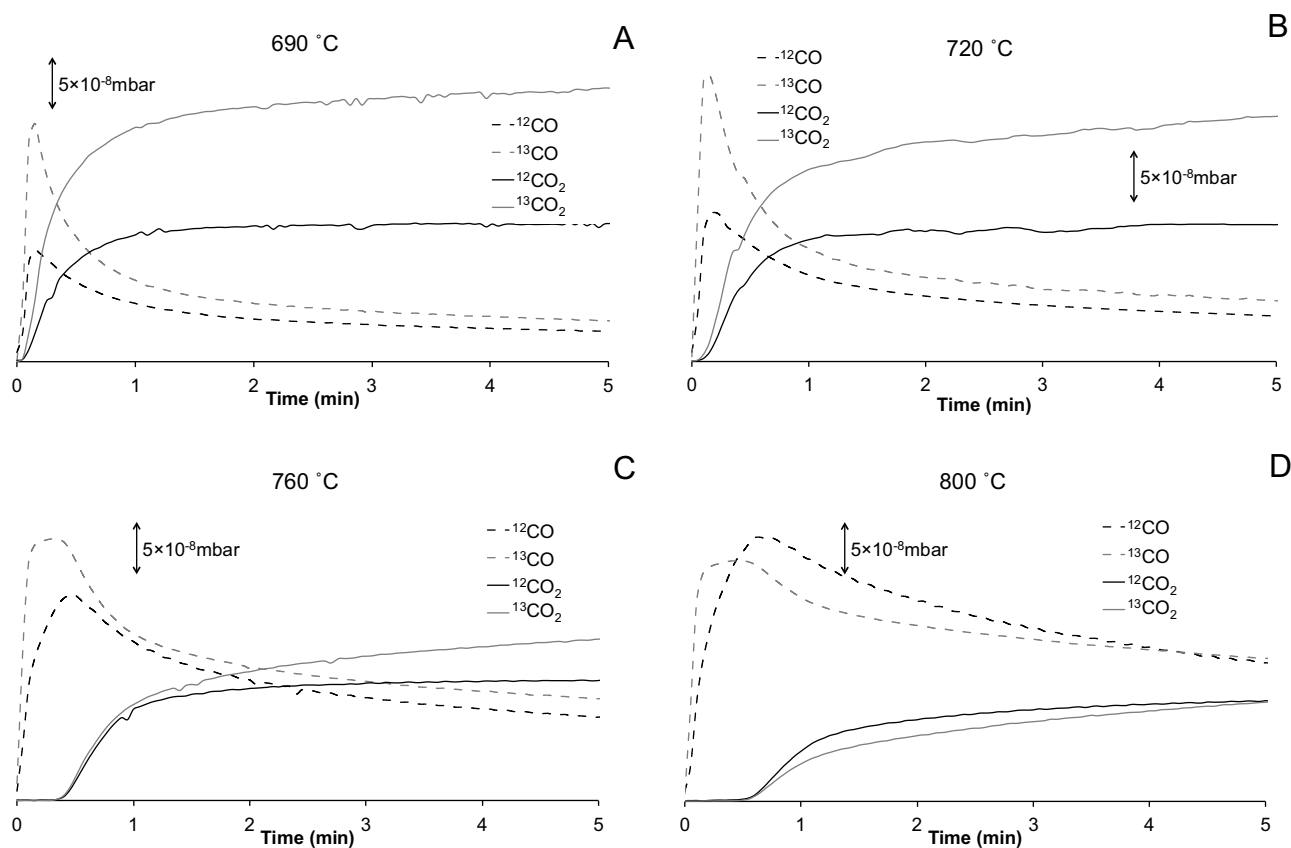
**Table 1**  
Catalysts general characterization.

|                                     | Metal loading (wt.%) | Metal loading surface <sup>a</sup> (%) | S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) | V <sub>Pore</sub> (cm <sup>3</sup> g <sup>-1</sup> ) | Coke loading (wt.%) | Coke loading (wt.% g m <sup>-2</sup> ) |
|-------------------------------------|----------------------|--|--|--|---------------------|--|
| Al <sub>2</sub> O <sub>3</sub>      | –                    | –                                      | 127  | 0.43   | 3 <sup>b</sup>      | 0.024                                  |
| Li/Al <sub>2</sub> O <sub>3</sub>   | 1.5 (Li)             | 5.6 (Li)                               | 48   | 0.23   | 1.9 <sup>b</sup>    | 0.040                                  |
| V/Al <sub>2</sub> O <sub>3</sub>    | 0.9 (V)              | 0.4 (V)                                | 122  | 0.44   | 7 <sup>b</sup>      | 0.057                                  |
| Li-V/Al <sub>2</sub> O <sub>3</sub> | 1.7 (Li)             | 6.9 (Li)                               | 46   | 0.22   | 3.9 <sup>b</sup>    | 0.085                                  |
|                                     | 0.9 (V)              | 0.2 (V)                                |  |  | 6.4 <sup>c</sup>    | 0.126                                  |
| USY                                 | –                    | –                                      | 605  | 0.24   | 18.1 <sup>c</sup>   | 0.030                                  |

<sup>a</sup> Determined through XPS analysis.

<sup>b</sup> Vacuum gasoil coke.

<sup>c</sup> 1,2:3,5-di-O-Isopropylidene-β-D-xylofuranose coke.



**Fig. 3.** <sup>12</sup>CO, <sup>13</sup>CO, <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> profiles for the Reverse-Boudouard reaction of gasoil coke deposited on the Li-V/Al<sub>2</sub>O<sub>3</sub> surface with <sup>13</sup>CO<sub>2</sub> (1.9%)/O<sub>2</sub> (0.8%)/He at 690 °C (A), 720 °C (B), 760 °C (C) and 800 °C (D).

coke is partially transformed in slow coke by the experiment conditions i.e. increasing the temperature from room to 700–800 °C in helium alters the coke composition and functionality. Considering coke complexity and its continuous transformation under in-situ condition it is beyond this work to extensively investigate the coke characterization.

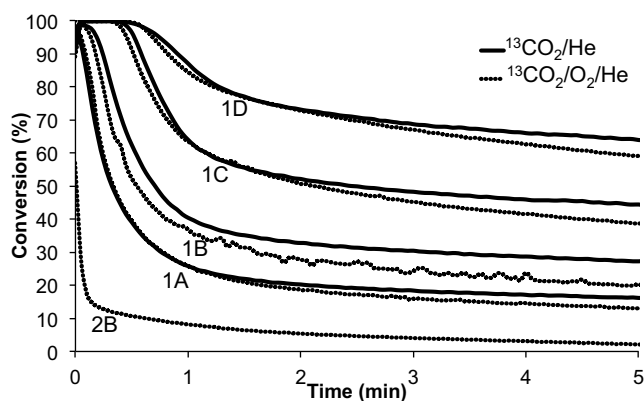
### 3.3. Reverse-Boudouard reaction at continuous-flow of <sup>13</sup>CO<sub>2</sub> at constant temperature

The Reverse-Boudouard reaction was carried out on spent Li-V/Al<sub>2</sub>O<sub>3</sub><sup>gasoil</sup> catalyst under continuous flow conditions at different temperatures compatible with FCC regenerator, i.e. 690 °C, 720 °C, 760 °C and 800 °C. In order to completely differentiate the CO formation resulting directly from RB reaction <sup>13</sup>CO<sub>2</sub> was used as reactant in the presence of helium or both oxygen and helium. Therefore <sup>13</sup>CO is directly related to <sup>13</sup>CO<sub>2</sub> conversion in the RB reaction through the following reaction: <sup>13</sup>CO<sub>2</sub> + Coke → <sup>13</sup>CO + Coke-O. On the other hand, <sup>12</sup>CO and <sup>12</sup>CO<sub>2</sub>

are related to coke burning through several consecutive reactions: Coke-O → <sup>12</sup>CO/<sup>12</sup>CO<sub>2</sub>, as presented elsewhere [20].

Fig. 2 shows the <sup>13</sup>CO<sub>2</sub>, <sup>13</sup>CO, <sup>12</sup>CO<sub>2</sub> and <sup>12</sup>CO profiles obtained during the first 5 min of spent Li-V/Al<sub>2</sub>O<sub>3</sub><sup>gasoil</sup> catalyst in <sup>13</sup>CO<sub>2</sub> (1.9%)/He atmosphere at 4 different temperatures. Firstly <sup>13</sup>CO formation is subtracted by <sup>13</sup>CO<sub>2</sub> fragmentation in MS (as explained in experimental section). At all temperatures <sup>13</sup>CO concentration quickly rises at short time on stream (TOS) and then decreases, being almost stable during 5 min of TOS. The formation of <sup>13</sup>CO was remarkably affected by temperature; higher reaction temperatures enable higher <sup>13</sup>CO formation (Fig. 2). This was followed by a greater consumption of <sup>13</sup>CO<sub>2</sub> resulting in 100% conversion for more than 30 s at 800 °C, after which conversion progressively decreased (as the <sup>13</sup>CO<sub>2</sub> concentration progressively increased) but during the recorded reaction time the conversion was relatively high. In a previous work it was demonstrated that disproportionation reaction did not take place (<sup>2</sup><sup>13</sup>CO → <sup>13</sup>C + <sup>13</sup>CO<sub>2</sub>) [43]. This fact is consistent with the complete <sup>13</sup>CO<sub>2</sub> conversion obtained at higher temperatures and low TOS, (<sup>13</sup>CO<sub>2</sub> + Coke → <sup>13</sup>CO + Coke-O). <sup>12</sup>CO formation





**Fig. 4.**  $^{13}\text{CO}_2$  conversion over  $\text{Li-V/Al}_2\text{O}_3^{\text{gasoil}}$  as function of reaction time for the Reverse-Boudouard reaction under  $^{13}\text{CO}_2$  (1.9%)/He or  $^{13}\text{CO}_2$  (1.9%)/ $\text{O}_2$  (0.8%)/He atmospheres. (A), (B), (C) and (D) represent the reaction temperature and stand, respectively, for 690 °C, 720 °C, 760 °C and 800 °C. (1) represents the catalytic tests using  $\text{Li-V/Al}_2\text{O}_3$  and (2)  $\text{Li/Al}_2\text{O}_3$ .

profiles differ from those of  $^{13}\text{CO}$  at lower temperatures becoming similar as temperature increases, i.e. increase at low TOS decreasing afterwards. Yet the maximum in  $^{12}\text{CO}$  formation is slightly dislocated compared to  $^{13}\text{CO}$  (Fig. 2 and Table S2). In contrast, the  $^{12}\text{CO}_2$  formation profile (a sequential product of RB reaction) largely differs from  $^{13}\text{CO}$  and  $^{12}\text{CO}$ . Its concentration quickly increased at lower TOS, continuing slowly increasing afterwards, phenomenon that becomes more evident at higher temperatures, i.e. 760 °C and 800 °C. We highlight that the higher the temperature the greater is the similarity between  $^{12}\text{CO}_2$  (production of RB reaction) and  $^{13}\text{CO}_2$  (unreacted in RB reaction).

Fig. 3 shows the  $^{13}\text{CO}_2$ ,  $^{13}\text{CO}$ ,  $^{12}\text{CO}_2$  and  $^{12}\text{CO}$  profiles obtained during the first 5 min of reaction between  $\text{Li-V/Al}_2\text{O}_3^{\text{gasoil}}$  under  $^{13}\text{CO}_2$  (1.9%)/ $\text{O}_2$  (0.8%)/He atmosphere at 4 different temperatures. Firstly, it is remarkable that  $^{13}\text{CO}_2$  shows a similar profile to that obtained with  $^{13}\text{CO}_2$ /He atmosphere. Secondly, as expected higher  $^{12}\text{CO}$  is formed due to the coke burning by  $\text{O}_2$ . In the particular case of  $^{12}\text{CO}$  the formed amount surpasses that of  $^{13}\text{CO}$  at 800 °C. Finally the amount of  $^{12}\text{CO}_2$  showed a similar profile for both atmospheres, i.e.  $^{13}\text{CO}_2$ / $\text{O}_2$ /He and  $^{13}\text{CO}_2$ /He, and followed the one observed to  $^{13}\text{CO}_2$  (unreacted). This phenomenon was also observed for the  $^{13}\text{CO}_2$ /He atmosphere and could be caused by two different facts: transformation of the formed  $^{12}\text{CO}_2$  into  $^{12}\text{CO}$  by Reverse-Boudouard reaction; preferential formation of CO compared to  $\text{CO}_2$  (particularly at higher temperatures) by the decomposition of oxygenated species in the coke (total TOS of 5 min).

The  $^{13}\text{CO}_2$  conversion into  $^{13}\text{CO}$  for both atmospheres, i.e.  $^{13}\text{CO}_2$  (1.9%)/He and  $^{13}\text{CO}_2$  (1.9%)/ $\text{O}_2$  (0.8%)/He, are represented in Fig. 4. As could be observed on Figs. 2 and 3, the  $^{13}\text{CO}_2$  conversion into  $^{13}\text{CO}$  largely increased at higher temperatures. The average conversion (for 5 min of TOS) for each temperature and both atmosphere are shown in Table 2. The presence of oxygen reduced the average conversion of  $^{13}\text{CO}_2$  less than 5%, and particularly at 800 °C profiles could not be distinguished (only 1.5% reduction was observed). The reduction on the  $^{13}\text{CO}_2$  conversion was quite small if considering that oxygen activity, as oxidant, is two orders of magnitude higher than that of  $\text{CO}_2$  [17,21]. In a previous work our group proved that the presence of oxygen had little impact in the  $^{13}\text{CO}_2$  reactivity using a  $\text{K-V/Al}_2\text{O}_3$  catalyst [19,20]. For the sake of comparison the conversion of  $^{13}\text{CO}_2$  at 720 °C over  $\text{Li/Al}_2\text{O}_3^{\text{gasoil}}$  using an atmosphere of  $^{13}\text{CO}_2$ / $\text{O}_2$ /He was included in Fig. 4. The average conversion during the first 5 min of reaction (Table 2) was only 6% for  $\text{Li/Al}_2\text{O}_3$  when compared to 33% showed by  $\text{Li-V/Al}_2\text{O}_3$  catalyst. Similar results were obtained for  $\text{V/Al}_2\text{O}_3$  with only 3% average conversion being achieved at 700 °C.

The ratio between  $^{12}\text{CO}$  and  $^{12}\text{CO}_2$  (formed during 5 min reaction) in both atmospheres is shown in Table 2. Without oxygen  $\text{CO/CO}_2$  varied from 0.6 to 11.4 and in the presence of oxygen from 0.6 to 9.1. The relative amount of  $^{12}\text{CO}$  formed was slightly reduced when oxygen was present. Despite this fact, the amount of  $^{12}\text{CO}$  produced at 800 °C in the presence of the atmosphere containing oxygen was 9 times higher than the amount of  $^{12}\text{CO}_2$ . On the other hand, the relative amount of  $^{12}\text{CO}$  obtained in  $\text{Li-V/Al}_2\text{O}_3$  catalyst at 720 °C was more than 7 times higher than that resulting from  $\text{Li/Al}_2\text{O}_3$ , respectively 1.6–0.2 in  $^{13}\text{CO}_2$ /He atmosphere. At 700 °C,  $\text{V/Al}_2\text{O}_3$   $^{12}\text{CO}$  to  $^{12}\text{CO}_2$  ratio was 0.4 under  $^{13}\text{CO}_2$ / $\text{O}_2$ /He atmosphere. The time observed in the maximum of  $^{12}\text{CO}$  formation as well as the time of inflexion point of  $^{12}\text{CO}_2$  (Table S2) differ around 30 s for both atmospheres (excluding the one at 690 °C for  $\text{CO}_2$ /He). These results strongly suggest that  $^{12}\text{CO}_2$  undergoes RB reaction producing  $^{12}\text{CO}$  as  $^{13}\text{CO}_2$  produces  $^{13}\text{CO}$ . Moreover the fact that  $^{12}\text{CO}$  did not coincide to the time of the inflexion point of the  $^{12}\text{CO}_2$  profile suggests that  $^{12}\text{CO}$  has the contribution of two reactions, regardless of the presence of  $\text{O}_2$ :  $\text{Coke-O} \rightarrow ^{12}\text{CO}/^{12}\text{CO}_2$ ; and  $^{12}\text{CO}_2 + \text{Coke} \rightarrow ^{12}\text{CO} + \text{Coke-O}$ . Coke-O decomposition into  $\text{CO}_2$  requires higher concentration of oxygenated species on the coke surface and is favored at lower temperatures while coke-O decomposition into CO is favored kinetically and thermodynamically at higher temperatures [44,45]. The combination of all these features makes the understanding of the profile of  $^{12}\text{CO}_2$  a complex task.

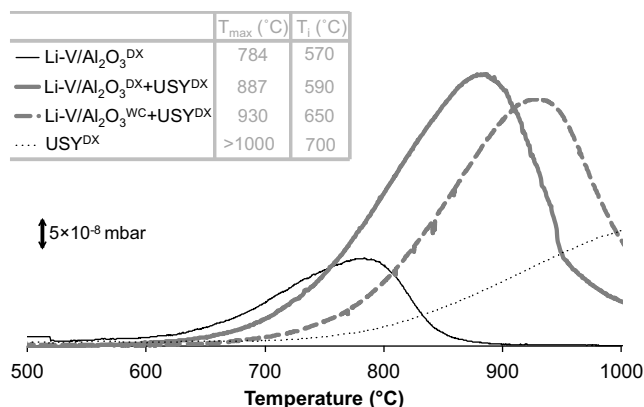
These results clearly indicate that not only the RB reaction is remarkably promoted by  $\text{Li-V/Al}_2\text{O}_3$  catalyst, but also that coke burning towards CO is largely improved regardless of the presence of oxygen; strongly suggesting that the regeneration step of the FCC process can be maintained under thermal equilibrium and convert  $\text{CO}_2$  into CO simultaneously. Previously Kelemen and Freund found that the enthalpy to perform the partial RB reaction (under high vacuum condition) varies from slightly exothermic to endothermic [17]. In addition this was support on the bases of the enthalpy of formation for several oxygenated compounds [22] that can provide energy for the partial RB reaction ( $\text{coke} + \text{CO}_2 \rightarrow \text{Coke-O} + \text{CO}$ ) that is able to produce oxygenate species in the coke. As partial RB reaction was remarkably improved even in the presence of  $\text{O}_2$  it should also be possible that the catalyst itself could transport energy from one point to another providing energy for partial RB reaction when required. To precise the nature and the amount of these coke-O species is beyond this work, however the presented results suggest that energy balance could be obtained by changing the partial pressure of  $\text{CO}_2$ / $\text{O}_2$  and the ratio additive/FCC catalyst.

### 3.4. Additive for Reverse-Boudouard reaction

The high efficiency of spent  $\text{Li-V/Al}_2\text{O}_3$  catalyst in RB reaction was demonstrated in the previous section. The addition of Vanadium or Lithium to the actual FCC catalyst is out of question, since both are poisons to the catalyst [39]. Yet,  $\text{Li-V/Al}_2\text{O}_3$  catalyst does not present the required properties to perform all the catalytic cracking reactions. However it could be used (prior to USY) in the cracking of larger molecules [46,47] or for others applications, as sulfur reduction [48] and metal trapping [49]. Vanadium undergoes migration under the FCC regenerator conditions. This phenomenon can favor the additive efficiency as the vanadium amount continually increases during the additive lifetime; thus decreasing the vanadium amount in the FCC catalyst and working as a vanadium trap. In order to be used as additive in the fluid catalytic cracking process (i.e. able to be used in a small amount compared to that of FCC catalyst) the  $\text{Li-V/Al}_2\text{O}_3$  has to fit three main features: to be able to promote the Reverse-Boudouard reaction improving the spent FCC catalyst regeneration in rich  $\text{CO}_2$  atmosphere; work

**Table 2**Average conversion and  $^{12}\text{CO}/^{12}\text{CO}_2$  ratio resulting from the Reverse-Boudouard reaction over  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{gasoil}}$ ,  $\text{Li}/\text{Al}_2\text{O}_3^{\text{gasoil}}$  and  $\text{V}/\text{Al}_2\text{O}_3^{\text{gasoil}}$  at different temperatures.

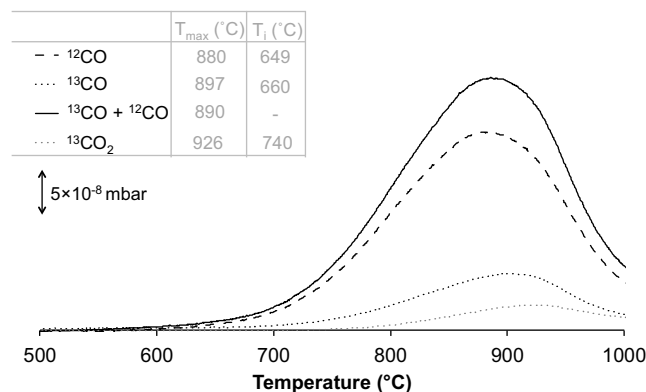
|   |     | $^{13}\text{CO}_2/\text{He}$ |                                   | $^{13}\text{CO}_2/\text{O}_2/\text{He}$ |                                   |
|---|-----|------------------------------|-----------------------------------|---|-----------------------------------|
|   |     | Conversion <sup>a</sup> (%)  | $^{12}\text{CO}/^{12}\text{CO}_2$ | Conversion <sup>a</sup> (%)             | $^{12}\text{CO}/^{12}\text{CO}_2$ |
| $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{gasoil}}$ | 690 | 25                           | 0.6                               | 23                                      | 0.6                               |
|   | 720 | 39                           | 1.6                               | 33                                      | 1.5                               |
|   | 760 | 58                           | 5.6                               | 55                                      | 3.2                               |
|   | 800 | 76                           | 11.4                              | 74                                      | 9.1                               |
| $\text{Li}/\text{Al}_2\text{O}_3^{\text{gasoil}}$   | 720 | 6                            | 0.2                               | ND                                      | ND                                |
| $\text{V}/\text{Al}_2\text{O}_3^{\text{gasoil}}$    | 700 | ND                           | ND                                | 3                                       | 0.4                               |

<sup>a</sup> Average conversion during the first 5 min of reaction.**Fig. 5.** CO formation profile for the Reverse-Boudouard reaction under increasing temperature ( $10^\circ\text{C min}^{-1}$ ) and 10%  $\text{CO}_2/\text{He}$  atmosphere.  $\text{Li-V}/\text{Al}_2\text{O}_3 + \text{USY}$  are representative of the mechanical mixture between  $\text{Li-V}/\text{Al}_2\text{O}_3$  and  $\text{USY}$  (1:1).  $T_{\text{max}}$  and  $T_i$  represent temperature for maximum CO formation and temperature at which CO begins to be formed. DX and WC stand respectively for samples with coke resulting from 1,2:3,5-di-*o*-isopropylidene- $\beta$ -D-xylofuranose and without coke.

in hydrothermal atmosphere; and in the presence  $\text{SO}_x$ . Herein the former feature is investigated.

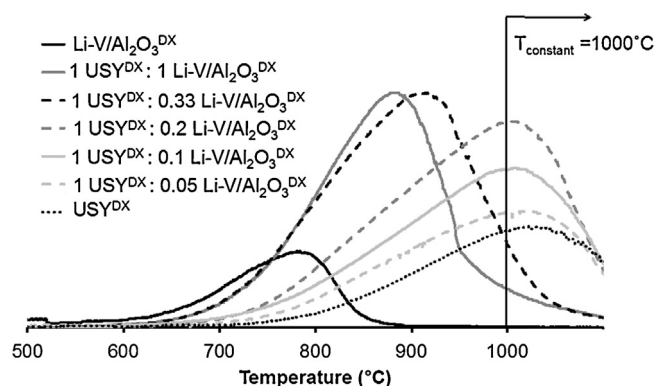
Spent  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  and spent  $\text{USY}^{\text{DX}}$  catalysts capacity to promote RB reaction was compared the performance of mixtures of these two samples in several proportions. Fig. 5 shows CO profiles obtained for the referred mixtures under  $\text{CO}_2$  (10%)/He flow in continuous increasing temperature (first experimental procedure in RB reaction, experimental section). This study was conducted in spent catalysts used in the cracking of a model mixture (DX and *n*-hexane). We highlight that coke nature did not significantly affected the RB reaction, as discussed previously. As expected spent  $\text{USY}^{\text{DX}}$  sample was quite inefficient in promoting the Reverse-Boudouard reaction with the maximum CO formation not being achieved before the temperature reached  $1000^\circ\text{C}$ . The samples composed of a physical mixture of  $\text{USY}^{\text{DX}}$  and  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  resulted in intermediate profiles between  $\text{USY}^{\text{DX}}$  and  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$ . For example a mixture of one to one part (in wt.%) of  $\text{USY}^{\text{DX}}$  and  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  resulted in a profile that achieved maximum CO formation at  $887^\circ\text{C}$ , whereas when pristine  $\text{Li-V}/\text{Al}_2\text{O}_3$  ( $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{WC}}$ —Without Coke) was mixed of one to one part of spent  $\text{USY}^{\text{DX}}$  the maximum in CO formation dislocated to  $930^\circ\text{C}$ . Similarly, the  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}} + \text{USY}^{\text{DX}}$  mixture was able to promote the Reverse-Boudouard reaction starting at lower temperature, i.e.  $590^\circ\text{C}$  compared to  $650^\circ\text{C}$  of  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{WC}} + \text{USY}^{\text{DX}}$  and  $700^\circ\text{C}$  of  $\text{USY}^{\text{DX}}$ . The results, shown in Fig. 5, clearly indicate that  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  is able to largely promote the Reverse-Boudouard reaction on the coke deposited on the  $\text{USY}$  surface in particular when coke is present on the  $\text{Li-V}/\text{Al}_2\text{O}_3$  surface.

An experiment using labeled coke ( $^{13}\text{C}$ ) on spent  $\text{USY}$  by means of labeled fructose (all carbons  $^{13}\text{C}$ ) was mixed up with spent  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  catalyst. These results are shown in Fig. 6. It is important to highlight that  $^{13}\text{CO}$  was formed at lower temperature than

**Fig. 6.**  $^{12}\text{CO}$ ,  $^{13}\text{CO}$ ,  $^{13}\text{CO}_2$  formation profile for the Reverse-Boudouard under increasing temperature ( $10^\circ\text{C min}^{-1}$ ) and 10%  $^{12}\text{CO}_2/\text{He}$  atmosphere. A mechanical mixture of  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$  and  $\text{USY}^{13\text{Coke}}$  (coke resulting from  $^{13}\text{C}$  labeled fructose) was used in the reaction.

observed on spent  $\text{USY}^{\text{DX}}$  (Fig. 5) as a consequence the formation of  $^{13}\text{CO}$  (that can only be originated from spent  $\text{USY}$ ) is direct evidence that  $^{12}\text{CO}_2$  reacts on  $\text{Li-V}/\text{Al}_2\text{O}_3^{\text{DX}}$ , producing  $^{12}\text{CO}$  and  $^{12}\text{Coke-O}$ . There are two possibilities to explain this results, vanadium can undergoes migration from additive to the spent  $\text{USY}$  or oxygen formed during partial RB reaction undergoes mobility (on coke or on the catalyst) to the spent ( $^{13}\text{Coke}$ )  $\text{USY}$  resulting in  $^{13}\text{CO}$  formation. Previously a commercial spent FCC catalyst containing vanadium and sodium, 5700 and 3600 ppm respectively, was evaluated in the RB reaction, showing a poor activity on the RB reaction with the activation occurring only at high temperatures [42]. Similar results were obtained on the spent  $\text{USY}$ . These observations suggest that vanadium migration (if occurring) between additive and  $\text{USY}$  could not play a dominant role in improving RB reaction. As a consequence on the base of these results it could be proposed that the additive improved the regeneration of spent catalyst through oxygen migration (from the additive to the catalyst), resulting in high CO selective compared to  $\text{CO}_2$ .

The proportion of this spent additive to the spent  $\text{USY}$  was explored (from 1:1 to 1:0.05 respectively) as presented in Fig. 7 and Table 3. In all the mixtures RB reaction starts at lower temperature than in spent  $\text{USY}$ , particularly for 1:1 and 1:0.33 proportions the maximum temperatures obtained were lower than  $1000^\circ\text{C}$ . As expected, when the proportion of additive decreases the effect on promoting the RB reaction becomes less evident and the CO formation profile becomes similar to that of spent  $\text{USY}$ . Furthermore, even when the proportion of additive is 20 times lower than of  $\text{USY}$  a slight effect on the promotion of RB reaction is observed, even if not all coke was burnt at the end of the experiment (Table 3). Despite this fact and considering that the typical reaction temperature for an FCC regenerator is around  $720^\circ\text{C}$ , the results show that  $\text{Li-V}/\text{Al}_2\text{O}_3$  can only work as additive in proportions of  $\text{USY}$  to promoter of 1–0.1.



**Fig. 7.** CO formation profile for the Reverse-Boudouard reaction under increasing temperature ( $10^{\circ}\text{C min}^{-1}$ ) and 10%  $\text{CO}_2/\text{He}$  atmosphere. y USY: y Li-V/ $\text{Al}_2\text{O}_3$  are representative of the mechanical mixture of x parts of USY to y parts of Li-V/ $\text{Al}_2\text{O}_3$  (in all cases the USY mass used was the same, i.e. 50 mg) DX stands for samples with coke resulting from 1,2:3,5-di-O-isopropylidene- $\beta$ -D-xylofuranose.  $T_{\text{max}}$  and  $T_i$  present in Table 3.

**Table 3**

Maximum and initial CO formation temperatures and final coke loading for Reverse-Boudouard reaction of mechanical mixtures of Li-V/ $\text{Al}_2\text{O}_3$  and USY under  $\text{CO}_2/\text{He}$  atmosphere and increasing temperature (CO profiles in Fig. 7).

|   | $T_{\text{max}}^{\text{a}}(^{\circ}\text{C})$ | $T_i^{\text{b}}(^{\circ}\text{C})$ | coke <sub>final</sub> (%)               |
|---|---|------------------------------------|---|
| Li-V/ $\text{Al}_2\text{O}_3$             | 784   | 570                                | traces <sup>c</sup> (6.4 <sup>d</sup> ) |
| 1 USY: 1 Li-V/ $\text{Al}_2\text{O}_3$    | 879   | 647                                | traces <sup>c</sup>                     |
| 1 USY: 0.33 Li-V/ $\text{Al}_2\text{O}_3$ | 913   | 647                                | traces <sup>c</sup>                     |
| 1 USY: 0.2 Li-V/ $\text{Al}_2\text{O}_3$  | >1000   | 688                                | traces <sup>c</sup>                     |
| 1 USY: 0.1 Li-V/ $\text{Al}_2\text{O}_3$  | >1000   | 655                                | traces <sup>c</sup>                     |
| 1 USY: 0.05 Li-V/ $\text{Al}_2\text{O}_3$ | >1000   | 682                                | 0.8                                     |
| USY                                       | >1000   | 706                                | 1 (19.1 <sup>d</sup> )                  |

<sup>a</sup> Temperature at which maximum CO formation was observed.

<sup>b</sup> Temperature at which CO starts to be formed.

<sup>c</sup> <0.1%.

<sup>d</sup> Initial coke loading.

### 3.5. Interpretation and speculation of catalytic sites responsible for promoting the Reverse-Boudouard reaction

The RB reaction on V-Li/ $\text{Al}_2\text{O}_3$  additives was rationalized in function of the distribution of coke and vanadium amount by the following considerations:

- The superficial vanadium amount is estimated in  $4\ \mu\text{mol/g cat.}$  (based on XPS results) while the coke loading is two orders of magnitude higher,  $325\ \mu\text{mol/gcat.}$
- Considering that the catalytic site is formed of, at least, one vanadium close to one lithium and that RB reaction is enhanced in the spent catalyst it could be possible that only a small amount of coke is in direct contact with both  $\text{CO}_2$  and V-Li active site under in situ conditions.

These two considerations lead to 24 molecules of  $^{13}\text{CO}_2$  reacting during the first 5 min reacts per 1 vanadium atom at  $800^{\circ}\text{C}$  that correspond to a TOF value of  $0.08\ \text{s}^{-1}$ . Similarly small TOF has been reported for reactions involving coke and  $\text{CO}_2$ . For instance, coke burning promoted by  $\text{MoO}_3$  addition resulted in a TOF value of  $0.25\ \text{s}^{-1}$  (estimated by the number of carbon atoms gasified per  $\text{CO}_2$  adsorbed per  $\text{MoO}_3$  site at  $500^{\circ}\text{C}$ ) and it was not affected by the size of particle [50]. In another work it was proposed that  $\text{CO}_2$  was activated in lanthanum oxide followed by its reaction with coke (formed on rhodium sites) with TOF varying from  $0.25$  to  $0.13\ \text{s}^{-1}$  at  $600$ – $527^{\circ}\text{C}$  respectively [51]. Despite several considerations the TOF value in this work for RB reaction is slight lower compared to the reported values in the literature. Obviously increasing the

vanadium ensemble corresponds to an equal increase in TOF, i.e. if the active site is composed of two vanadium atoms TOF is doubled. However,  $\text{CO}_2$  adsorption is proposed to occur in simple sites [17,52]. Likewise XPS could not account to all vanadium on surface.

Additionally to the aforementioned consideration tests performed under increasing temperature (Fig. 1) and Table 3 or performed in no labeled  $\text{CO}_2$  (results not shown) during longer time on stream led to complete coke consumption. This was clearly related to oxygen species mobility, but solely oxygen mobility cannot respond to the burning of all the coke as it is necessary a continuing activation of  $\text{CO}_2$ , which should happen in a V-Li site in close proximity to coke. Firstly taking in consideration the aforementioned points it could be proposed that under these conditions either vanadium or coke could undergo mobility. The latter has never been reported while vanadium mobility is observed under FCC process [39,53,54]. Several vanadium compounds have melting point around  $700^{\circ}\text{C}$  and yet it has been demonstrated that vanadium can be oxidized to +5 by either  $\text{CO}_2$  [55] or  $\text{O}_2$  [40]. Secondly the augmentation observed in coke formation on the catalyst, in particular when Vanadium is present, suggested that coke would undergo reaction with  $\text{CO}_2$  from bottom to the top of coke layers, as previously proposed [50]. Moreover, considering the small amount of vanadium available on the catalyst surface it should also be possible that  $\text{CO}_2$  diffusion to the active sites is limited, as the active sites are placed below a pile of coke, both phenomena (vanadium mobility and diffusion) could account to lowering the TOF value.

### 3.6. Outlook

It was proposed in our previously work that regular FCC unit could be adjusted to work in auto-thermal conditions performing RB reaction by controlling the partial pressure of  $\text{O}_2$  and  $\text{CO}_2$  [19,20]. In addition the FCC regenerator could be retrofitted including a second step devoted to burning the residual coke from the incomplete coke consumption under an atmosphere rich in  $\text{CO}_2$ . Moreover these steps could work using diathermic walls in order to transfer heat from the second step to the first one, maintaining the heat balance of the process. Herein it was shown that a vanadium lithium alumina catalyst is an efficient additive for promoting the RB reaction in the presence of  $\text{CO}_2$  and  $\text{O}_2$ . Simultaneously, the same type additive can be properly used for sulfur reduction [48,56]. This additive works up to one to ten parts of catalyst, but the higher the amount of additive the better the improvement in RB reaction. Obviously in terms of a regular FCC unit higher amounts of additive imply a decrease in the processed feed. However we anticipate that in a near future an increase in the coke amount in the spent catalyst of some FCC units is expected. This is related to both the tendency of processing higher amount of lower quality feedstock and the possibility of introducing non-conventional feeds, like pyrolysis bio-oil for example [15]. In that case alumina based catalysts could be tailor made to the cracking of large molecules (in the riser) and promote the RB reaction in the regeneration step. Therefore in this scenario higher amounts of additive could be acceptable resulting in a huge amount of  $\text{CO}_2$  mitigation.

## 4. Conclusion

Vanadium lithium alumina catalyst is an efficient additive for performing the regeneration of a spent catalyst under FCC conditions in  $\text{CO}_2$  rich atmosphere regardless the presence of  $\text{O}_2$ . Moreover RB reaction seems to be less affected by the type of coke on this catalyst.

RB reaction is favored in an ensemble containing lithium and vanadium and coke and proceeds by forming CO and oxygenated species in the coke, which degrade forming CO and  $\text{CO}_2$ . The lat-



ter sequentially reacts producing more CO; therefore this catalyst largely increased the CO/CO<sub>2</sub> ratio. Moreover, it was proven that Li-V/Al<sub>2</sub>O<sub>3</sub> could also work as an additive to the FCC catalyst as it was able to promote coke burning in spent USY, in particular when coke is deposited on Li-V/Al<sub>2</sub>O<sub>3</sub> surface. This was related to oxygen mobility, which was enhanced when coke is in the vicinity of the active site. The additive effect was considered efficient up to 1 part of additive to 10 parts of USY.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.05.024>.

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